PATENT SPECIFICATION

632,955

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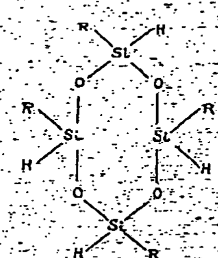
COMPLETE SPECIFICATION

Improvements in and relating to Polysiloxanes

We, THE BRITISH THOMSON-HOUSTON COMPANY LIMITED, a British Company having its registered office at Crown House, Aldwych, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new and useful chemical compounds, and more particularly is concerned with compounds known as polysiloxanes. Specifically the invention relates to new cyclopolysiloxanes corresponding to the general formula $(RSiHO)_n$, where R represents a lower alkyl radical (e.g., methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, *sec*.-butyl), and *n* represents 4, 5 or 6, and to methods of preparing such cyclopolysiloxanes. Cyclopolysiloxanes corresponding to, for example, the general formula $(RSiHO)_4$, where R represents a lower alkyl radical, also may be represented by the formula



In a similar manner structural formulas for cyclopolysiloxanes corresponding to the general formulas $(RSiHO)_5$ and $(RSiHO)_6$, that is cyclopolysiloxanes containing 5 or 6 Si atoms linked with oxygen atoms in a ring structure, may be written.

It was known prior to the invention that cyclic compounds having the formula $[(CH_3)_2SiO]_n$, where *n* is an integer which is at least 3 and not more than 10 could be prepared, for example by heating the higher boiling polymers of dimethyl silicone having the formula $[(CH_3)_2SiO]_n$, where *n* is an integer greater than 10, at an elevated temperature (above 200° C.) in a non-oxidizing atmosphere. Such cyclic silicon compounds are more fully described in British Specification No. 686,188. The compounds of the present invention, more particularly cyclopolysiloxanes corresponding to the general formula $(CH_3SiHO)_n$, where *n* represents 4, 5 or 6, differ from those disclosed in the aforementioned specification, in that, instead of two methyl groups being attached directly to each nuclear Si atom, there are attached thereto one methyl group and one hydrogen atom.

The cyclopolysiloxanes of this invention are especially valuable as intermediates in the preparation of other organo-silicon compounds for instance linear polysiloxanes of the kind disclosed in copending application No. 7700/47 (Serial No. 632,954). These cyclic compounds, specifically the symmetrical polymethylcyclopolysiloxanes, also are useful in making other new organo-polysiloxanes, more particularly oils of improved viscosity-temperature coefficient.

The cyclopolysiloxanes with which this invention is concerned may be prepared by causing a halogenosilane corresponding to the general formula $RSiHX_2$, where R represents a lower alkyl radical and X represents chlorine or bromine, to react with water (i.e., to be hydrolyzed) whereby there are obtained cyclopolysiloxanes corresponding to the general formula $(RSiHO)_n$, where R has the meaning above given and *n* represents 4, 5 or 6 and isolating the said cyclopolysiloxanes, e.g. by distillation, from the resulting reaction mass. The halogenosilanes used in practising this method

may be produced, for example, by the interaction of a lower alkyl magnesium halide, e.g., ethyl magnesium chloride, or propyl magnesium bromide with trichlorosilane, $HSiCl_3$, or tribromosilane, $HSiBr_3$. In these reactions approximately one mole of the appropriate Grignard reagent dissolved in ether is used for each mole of the trihalogenosilane, and the Grignard solution is added slowly to the trihalogenosilane. Examples of halogenosilanes that may be prepared in this way are the methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, and *sec*-butyl, dichloro and dibromo silanes ($RSiHCl_2$ and $RSiHBr_2$).

Although an oil of about 20—25 centistokes viscosity usually results when, for instance, dimethyldichlorosilane is hydrolyzed by adding it directly to water or to a mixture of ice and water, a somewhat different result is obtained with methyldichlorosilane, CH_3SiHCl_2. The product first formed is a highly viscous oil which is transformed in a few minutes into an opalescent, sticky, rubbery gel.

Surprisingly it was found that halogenosilanes corresponding to the general formula $RSiHX_2$ where R and X have the meaning given in the preceding paragraph, particularly methyldichlorosilane, can be so hydrolyzed (e.g., at a temperature of minus 10° to plus 15° C.) as to obviate the relatively rapid formation of a polymer (rubbery gel) of high molecular weight and to yield cyclopolysiloxanes of the kind set forth in the first paragraph of this specification, which cyclopolysiloxanes can be separated from the reaction mass in the form of substantially pure compounds by fractional distillation technique. This result is obtained by admixing the halogenosilane and a cold mixture of water (or ice) and an organic diluent which is insoluble or substantially insoluble in water, more particularly by slowly adding the halogenosilane, e.g., methyldichlorosilane, to said mixture of water (or ice) and organic diluent while vigorously stirring the mixture. Examples of inert organic diluents that may be employed in this way are diethyl ether, dipropyl ether, benzene, and low-boiling petroleum fractions. Instead of water alone, we may use alcohol-water mixtures, for instance mixture of water and, for example, methanol, ethanol, propanol, butanol, mixed amyl alcohols, *n*-hexyl alcohol. The inert organic diluent or mixture thereof with an alcohol appears to increase the proportion of cyclopolysiloxanes that are formed and suppresses their polymerization by reducing the concentration of halogen acid in the reaction mass.

It was not known prior to the invention and in no way could have been predicted that a lower alkyl dichloro or dibromo silane could be caused to yield cyclopolysiloxanes of the kind with which this invention is concerned upon reaction with a hydrolysis medium comprising water. The unobvious nature of the discovery will better be appreciated when it is considered that some prior investigators have considered that the liquid products obtained by the hydrolysis of a dimethyldihalogenosilane, specifically dimethyldichlorosilane, consist primarily of long chain molecules and a small amount of a cyclic trimer, $[(CH_3)_2SiO]_3$ (Hyde and DeLong, Journal of the American Chemical Society, *63*, 1194—6). It also is pointed out in the aforementioned Specification No. 586,188 that the cyclic trimer, $[(CH_3)_2SiO]_3$, is one of the constituents of the product of hydrolysis of dimethyldichlorosilane with a quantity of water substantially in excess of that calculated as necessary for complete hydrolysis of the said dichlorosilane. In marked contrast, no trimethylcyclotrisiloxane (*sym.* - trimethylcyclotrisiloxane), $(CH_3SiHO)_3$, was found in the product we obtained by a somewhat similar treatment of methyldichlorosilane, more particularly by adding methyldichlorosilane to a mixture of diethyl ether and water in the form of cracked ice, the latter representing an amount of water substantially in excess of that theoretically required for complete hydrolysis of the methyldichlorosilane, and stirring the reaction mass for a further period after the addition of the aforesaid lower alkyl dichlorosilane.

A surprising characteristic of the cyclopolysiloxanes of the invention as compared with the cyclic polymers of dimethyl silicone described in the aforementioned application is that the reactivity of the siloxane linkages in polymerization reactions is apparently enhanced, as evidenced by the fact that 1,3,5,7, - tetramethylcyclotetrasiloxane, which normally is a liquid is converted to a solid by agitating it with 20% aqueous hydrochloric acid for three hours. The hydrochloric acid apparently cleaves the siloxane linkages with such ease that a high-molecular weight cyclic polymer containing the unit structure

$$-\overset{\displaystyle R}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O-$$

and having a composition corresponding substantially to the formula

$(CH_3SiHO)_n$, where n represents a large whole number (possibly 15 to 30 or more) is formed. The greater reactivity of the siloxane linkages in the compounds of the invention, e.g., the methyl derivatives, as compared with the corresponding cyclic polymers of dimethyl silicone, is further shown by the fact that they polymerize to semisolid or solid bodies on standing for a prolonged period, e.g., 9 to 12 months or more, at room temperature while exposed to air and light. The enhanced reactivity of the siloxane linkages in the new compounds may be due to diminution of the steric hindrance of the groups attached to silicon since the hydrogen atom is smaller than a methyl group.

In order that those skilled in the art better may understand how the present invention may be carried into effect, the following examples are given by the way of illustration and not by way of limitation:

EXAMPLE 1.

Four moles (460 g.) of methyl dichlorosilane, b.p. 41.3° C. (760 mm.), 61.4% Cl, was added with vigorous stirring to a mixture of 1 liter of diethyl ether containing a small amount of benzene, and 2 kilograms of cracked ice over a half-hour period. The temperature of the hydrolyzing mixture dropped from 0° C. to minus 10° C., but rose finally to plus 7° C. After stirring for an additional half hour the aqueous layer was separated and the organic phase washed (three times with water until it was neutral to methyl orange. After removal of the ether and the small amount of benzene, the product was fractionated by distillation first at atmospheric pressure and then under reduced pressure as the temperature of distillation was increased. By this distillation there was obtained, by weight, about 36% of 1, 3, 5, 7,-tetramethylcyclotetrasiloxane, b.p. 134.5 134.9° C. (755 mm.), about 17% of 1,3,5,7,9 - pentamethylcyclopentasiloxane, b.p. 168.6—168.9° C. (755 mm.), and about 4½% of impure 1,3,5,7,9,11-hexamethylcyclohexasiloxane, b.p. 92.6 93° C. (21 mm.) together with forerunnings and intermediate fractions amounting to about 14½% and a residue of about 28%. No effort was made to identify the composition of this residue. However, it is possible that it comprised a mixture of 1,3,5,7,9,11,13 - heptamethylcycloheptasiloxane, 1,3,5,7,9,11,-13,15 - octamethylcyclooctasiloxane, 1,3,5,7,9,11,13,15,17, - nonamethylcyclononasiloxane and higher homologues, as well as other compounds. The impure hexamethyl derivative was refractionated to obtain a purer material having a boiling point of 76—77° C. at 10.2 mm. pressure. Other data on the characteristics of the tetramer, pentamer and hexamer (purified material) are given in the following table:

TABLE I.

	n_D^{20}	d_4^{20} (vac.)	R_D	m.p. (° C.)	Mol. Wt. Calculated	Mol. Wt. Found*	%H (attached to Si)** Found
Tetramer	1.3870	0.9912	0.2375	-69 ± 3	240.4	239, 241, 244	1.64, 1.64
Pentamer	1.3912	0.9983	0.2381	-108 ± 3	300.5	298, 297, 297	1.65
Hexamer	1.3944	1.006	0.2380	-79 ± 2	360.6	360	1.67

* Cryoscopic in cyclohexane; maximum concentration of solute in weight per cent.: tetramer, 0.56; pentamer, 0.72; hexamer, 0.78.

** Theoretical for CH_3SiHO, 1.68.

In separating the above-described cyclopolysiloxanes by distillation from the hydrolyzate, the distillation took place under non-oxidizing or substantially non-oxidizing conditions since the forerunnings swept the distillation apparatus free or substantially free from air. In this way oxidation of the hydrolyzate and of the compounds distilled therefrom during distillation was obviated or minimized.

In a manner similar to that described above with particular reference to the preparation of 1,3,5,7-tetramethylcyclo-

dichlorosilane with a quantity of water cyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane, other lower alkyl cyclopolysiloxanes of similar structure may be obtained by hydrolyzing the corresponding lower alkyl dichloro or dibromo silanes, examples of which have been given hereinbefore, and isolating the resulting cyclopolysiloxanes from the oily hydrolyzate.

In a manner similar to that hereinbefore described with particular reference to the preparation of 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane, other cyclopolysiloxanes embraced by the general formula $(RSiHO)_n$, where R represents a lower alkyl radical and *n* represents 4, 5 or 6, may be prepared and thereafter polymerized. Examples of such compounds and polymers thereof are:

1,3,5,7-tetraethylcyclotetrasiloxane
1,3,5,7-tetrapropylcyclotetrasiloxane
1,3,5,7-tetraisopropylcyclotetrasiloxane
1,3,5,7-tetra-*n*-butylcyclotetrasiloxane
1,3,5,7-tetraisobutylcyclotetrasiloxane
1,3,5,7-tetra-*sec.*-butylcyclotetrasiloxane
1,3,5,7,9-pentaethylcyclopentasiloxane
1,3,5,7,9-pentapropylcyclopentasiloxane
1,3,5,7,9-pentaisopropylcyclopentasiloxane
1,3,5,7,9-penta-*n*-butylcyclopentasiloxane
1,3,5,7,9-pentaisobutylcyclopentasiloxane
1,3,5,7,9-penta-*sec.*-butylcyclopentasiloxane
1,3,5,7,9,11-hexaethylcyclohexasiloxane
1,3,5,7,9,11-hexapropylcyclohexasiloxane
1,3,5,7,9,11-hexaisopropylcyclohexasiloxane
1,3,5,7,9,11-hexa-*n*-butylcyclohexasiloxane
1,3,5,7,9,11-hexaisobutylcyclohexasiloxane
1,3,5,7,9,11-hexa-*sec.*-butylcyclohexasiloxane and polymers thereof.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The method of preparing cyclopolysiloxanes which consists in slowly adding a lower alkyl dichloro silane with vigorous stirring to a cold mixture of an inert organic diluent and water, stirring the reaction mass for a further period after the addition of all of the lower alkyl dichloro silane, and separating cyclopolysiloxanes corresponding to the formulas $(RSiHO)_4$, $(RSiHO)_5$ and $(RSiHO)_6$ from the organic phase containing the same.

2. The method of preparing cyclopolysiloxanes which consists in slowly adding methyldichlorosilane with vigorous stirring to a mixture of diethyl ether and ice, stirring the reaction mass for a further period after the addition of all of the methyldichlorosilane, washing the organic phase comprising diethyl ether with water until it is substantially neutral, and separating by distillation from the washed organic phase cyclopolysiloxanes represented by the formulas $(CH_3SiOH)_4$, $CH_3SiOH)_5$ and $(CH_3SiHO)_6$.

3. A cyclopolysiloxane prepared by the method claimed in Claim 1 or 2 corresponding to the general formula $(RSiHO)_n$, where R represents a lower alkyl radical and *n* represents 4, 5 or 6.

4. A cyclopolysiloxane prepared by the method claimed in claim 1, 2 or 3 corresponding to the general formula $(CH_3SiHO)_n$, where *n* represents 4, 5 or 6.

5. A method according to Claim 1 or 2, in which the corresponding bromosilane is used instead of the chlorosilane.

Dated this 13th day of March, 1947.

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